NASA Research Publication 1402

SAMPR: A Computer Code for Simple Analysis of Materials Processing Reactors

M. Meyyappan, Ames Research Center, Moffett Field, California
T. R. Govindan, Applied Research Laboratory, State College, PA

April 1997

National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035-1000

Abstract

This is the user's manual for a computer code (SAMPR: Simple Analysis of Materials Processing Reactors) that solves zero-dimensional or volume-averaged conservation equations for the analysis of plasma and non-plasma reactors used in semiconductor processing. Species mass, gas energy, and electron energy equations are solved taking into account homogeneous reactions. Surface reactions are also taken into account in the species balance through properly weighting by the surface-to-volume ratio.

Contents

SAMPR: A Computer Code for Simple Analysis of Materials Processing Reactors

1. Introduction

This document serves as user's manual for the computer code SAMPR (Simple Analysis of Materials Processing Reactors). The code is meant for the analysis of plasma and non-plasma processes used in semiconductor manufacturing; however it may be used to analyze any chemical processing reactor dealing with gaseous (but not liquid) streams. The model consists of balance equations for the total mass, mass of individual species, and gas energy. In the case of plasma reactions, a plasma power balance is also included. The balance equations are reactor volume-averaged or in other words represent a zero-dimensional (0 - d) analysis. For this analysis to be valid, the reactor contents must be well mixed and not exhibit significant gradients of species concentrations or gas temperature in any part of the reactor. Such perfect mixing conditions may be found in reactors used in chemical process industries; several text books on reaction kinetics discuss the operation of Continuous Stirred Tank Reactors (CSTR), see for example in ref. 1. Such ideal conditions may not exist in reactors used for etching, deposition, annealing or performing any other functions in the course of integrated circuit manufacturing. Nevertheless, approximate solutions to somewhat idealized reactor conditions may be valuable in estimating overall conversion efficiency of feedstock, effluent concentrations, and energy utilization. A good example of this utility can be found in the development of 0 - d or global analysis of various plasma sources used for etching and deposition of thin films [2 - 4]. The analysis provides volume-averaged electron density, electron temperature, and radical and ion concentrations as functions of pressure, input power, and flow rates. Obviously, detailed information on the uniformity of plasma, and radical and ion fluxes near the wafer is lost in such a global model, but qualitative behavior of the plasma as a function of system parameters or the so-called "scaling laws" can be obtained very rapidly. Generation of such valuable knowledge with minimal computational resources is the attraction of this simple approach. Also, the results of a 0-d model can provide guidance for further multidimensional simulations. In semiconductor processing

situations, the number of species and reaction pathways is usually large. Multidimensional analysis with a large reaction and species set is computationally intensive. A 0-d analysis in that case can be effectively used in a systematic study to generate a "reduced chemistry set" that provides reasonable results.

This manual is organized as follows. The next section discusses the balance equations and the limitations of the approach. This is followed by a brief description of the numerical method used to solve the nonlinear algebraic equations. The references cited are listed in section 3. A detailed description of the function of various subroutines, and explanation of input variables and output format are provided in section 4. Application of the code to some problems of interest with sample input and output files is given in section 5.

2. Model

The model development below is generalized to consider a nonequilibrium plasma reactor where the electrons and neutral species are not at thermodynamic equilibrium. At present, the ion temperature is assumed to be equal to the gas temperature. Conservation equations under the above assumption for the mass of individual neutrals and ions, gas energy balance, and plasma power balance are written. For non-plasma reactors, the ion density and plasma power balance equations are ignored; this is facilitated by the use of a logic variable called "plasma" in the input. The users interested in nonplasma problems may ignore references to two temperatures and other plasma related discussion below and follow only the species conservation and gas energy balance.

We consider a plasma source chamber of radius r, length L, and volume V ($=\pi r^2 L$) where the plasma is generated. The total surface area A may consist of wall (A_s) and wafer (A_w) areas. The wafer may be processed in the source chamber or in a separate process chamber. If there is a separate process chamber downstream, it may be analyzed in a cascading fashion, i.e. process chamber inflow conditions will be the outflow properties computed in the source chamber analysis. This is facilitated by a logic variable "cascade." Further discussion on cascading will be provided later.

It is not easy to include the nature and details of power deposition, associated magnetic field effects, etc. in a zero-dimensional volume-averaged model; plasma power input is simply treated as a model input variable. In this sense, there is nothing in the model that distinguishes ICP and ECR reactors and what follows is an analysis of a generic high density plasma reactor. The approach presented below is not adequate for analyzing rf capacitively coupled reactors. A simple lumped parameter input for power is not enough in this case and also time variation of electron density within the cycle in response to the rf power needs to be considered. Further discussion on the modeling needs of rf plasmas can be found in Aydil and Economou [4]. SAMPR can be modified to include the additional details in ref. [4] to apply to rf capacitive plasmas.

2.1. Species mass conservation

A mass balance for each of the neutral and ionic species in the plasma is written as

$$\rho V \frac{dy_i}{dt} = \dot{m}\ (y_{i,in} - y_i) + VM_i \sum_j R_{ij} + AM_i \sum_k S_{ik} \qquad i = 1, I \tag{1}$$

Here, the subscript in denotes inlet conditions. I is the total number of neutral and ionic species. y_i is the mass fraction of species i ($y_i = \rho_i / \rho$) ; ρ_i is the mass density of species i given by $n_i m_i$ where n_i and m_i are the species number density and mass. Other notations are as follows. $\dot{m}$ is the total mass flow rate; M_i is the molecular weight; R_{ij} is the molar homogeneous reaction rate of species i in reaction j ; S_{ik} is the molar heterogeneous reaction rate of species i in surface reaction k. The terms on the right side of eqn (1) represent changes due to the flow, and species production/ consumption due to the volume and surface reactions, respectively. In principle, the last term in eqn (1) can be written as two independent contributions from wall and wafer reactions as they differ in nature. The net rate of production from volume reactions R_{ij} is written as

$$R_{ij} = \left(v_{ij}'' - v_{ij}'\right) \left[k_{fi} \prod_{i=1}^{i=I} (\rho y_i / M_i)^{v_{ij}'} - k_{rj} \prod_{i-1}^{i=I} (\rho y_i / M_i)^{v_{ij}''} \right] \tag{2}$$

Here v_{ij} is stoichiometric coefficient of species i in reaction j. The single and double primes denote reactant and product, respectively. k_{fj} and k_{rj} are forward and reverse rate coefficients for elementary reaction step j . The surface reaction rate is written in a similar manner.

The mass flow rate $\dot{m}$ in eqn (1) is taken as constant, though in principle, surface reactions may result in a loss of mass. In such a case, the first term in eqn (1) would be written as $\dot{m}_{in}\, y_{i,in} - \dot{m}\, y_i$, and $\dot{m}$ then can be obtained from a total mass balance which is the sum of eqn (1) over all I species:

$$\dot{m}_{in} - \dot{m} + A \sum_i M_i \sum_k S_{ik} = 0 \tag{3}$$

The plasma is assumed to be neutral and thus, the electron number density is obtained from

$$n_e = \sum_{i=1}^{I} q_i n_i \tag{4}$$

where q_i is the charge of species i.

2.2. Thermodynamic relation

The gas density, ρ, is computed from the thermodynamic relation:

$$p = \sum_{i \neq e} p_i + \sum p_e$$

$$= RT_g \rho \left[\sum_{i \neq e} \frac{y_i}{M_i} + \frac{T_e}{T_g} \frac{y_e}{M_e} \right] \tag{5}$$

where p is the total reactor pressure, R is the universal gas constant, T_g is the gas temperature, and T_e is the electron temperature. The second term due to the electrons is usually negligible in diode reactors since the plasma is very weakly ionized. In contrast, fractional ionization n_e/n may be of $O(10^{-2})$ in high density discharges with T_e/T_g nearly of $O(10^2)$. n is total number density in the reactor. Hence, contribution of electron pressure to the total cannot be ignored, especially at low pressures and high power levels. In principle, the thermodynamic relation in (5) may be written to recognize an ion temperature also, however the effect is expected to be negligible. In any case, currently we assume that the ion temperature is the same as that of the gas.

2.3. Plasma power balance

The power balance in the plasma source takes the form:

$$P_{ext} = P_e + P_{ion} \tag{6}$$

where P_{ext} is the external applied power, and P_e and P_i are power deposited to electrons and ions, respectively. While it is possible to express P_e in terms of electron conduction current and average electric field, we obtain P_e from an electron energy balance assuming that the electron-ion volume recombination is negligible:

$$\left(Qn_e\varepsilon_e\right)_{in} - Qn_e\varepsilon_e + P_e - V\tilde{N}\sum_j R_{ej}H_j$$

$$-3\left(\frac{m_e}{m}\right)\nu_{el}Vn_e k\left(T_e - T_g\right)$$

$$-A\Gamma_e\left(\varepsilon_e + 0.5kT_e\right) = 0 \qquad (7)$$

Here Q is flow rate given by $\dot{m}/\rho$, ε_e is electron mean thermal energy $\left(= 3/2kT_e\right)$ where k is Boltzmann constant, $\tilde{N}$ is Avagodro number, R_{ej} is rate of electron impact reaction j, H_j is the corresponding threshold energy, m is mixture-average mass, ν_{el} is the elastic collision frequency, and Γ_e is electron wall flux. The terms in eqn (7) represent electron energy from inflow and outflow, energy gain from external source, energy loss from all inelastic collisions, energy loss from elastic collisions, and energy lost due to electron wall recombination, respectively. The energy of electrons at the wall is $\varepsilon_e + 1/2m\,\mathrm{v}^2$ where v is electron directed velocity; we assume that the electrons at the wall are thermal and rewrite their energy as $\varepsilon_e + 0.5kT_e$. The electron wall flux Γ_e must equal the positive ion wall flux, assuming that the massive negative ions are excluded from the wall due to the positive plasma potential.

$$\Gamma_e = \sum\Gamma_+ = \left(A_{eff}/A\right)\sum n_+ u_{B,+} \qquad (8)$$

Here, the subscript + indicates a positive ion and Σ indicates sum over all positive ions. u_B is the Bohm velocity given by $\left(kT_e/m_+\right)^{0.5}$. Implicit in eqn (8) is the assumption that the ion flux Γ_+ at the wall is the same as that at the edge of the sheath. A_{eff} is an effective area as suggested in ref. 3 to account for the deviation of sheath edge ion density from that at the center.

$$A_{eff} = A_R h_R + A_L h_L \qquad (9)$$

where A_R and A_L are radial and axial surface areas. The correction factors h_R and h_L are from the work of Godyak [5] and as used by Lee and Liberman [3]:

$$h_R = 0.8/(4.0 + r/\lambda)^{0.5}$$
$$h_L = 0.86/(3.0 + 2L/\lambda)^{0.5} \tag{10}$$

where λ is the mean free path based on charge exchange collisions. h_r and h_L reduce to 0.4 and 0.5 at the free fall limit. The correction factor in eqn (10) is appropriate for inert gases. Further modifications are provided for reactive gases and mixtures by Lee and Liberman [3] which have not been included yet in SAMPR.

The ion power deposition, P_{ion}, is given by

$$P_{ion} = A\sum \Gamma_+ \Delta\Psi \tag{11}$$

where $\Delta\psi$ is the driving potential equal to the difference between the plasma and wall potentials. $\Delta\psi$ can be estimated from eqn (8) by recognizing that

$$\Gamma_e = (n_e/4)v_{e,th}\exp(-\Delta\Psi/kT_e) \tag{12}$$

where $v_{e,th}$ is electron thermal velocity, $(8kT_e/\pi\, m_e)^{0.5}$. Combining eqns (8) and (12) we get

$$\Delta\Psi = -KT_e \cdot ln\left[\frac{(A_{eff}/A\sum n_+ u_{B+})}{(n_e/4)v_{e,th}}\right] \tag{13}$$

Combining eqns (6), (7), (8), (11) and (12), we get the final form of the power balance:

$$1.5V\frac{d(nkT_e)}{dt} = P_{ext} + (Qn_e\varepsilon_e)_{in} - Qn_e\varepsilon_e - V\tilde{N}\sum_j R_{ej}H_j$$
$$-3(m_e/m)\nu_{el}Vn_e k(T_e - T_g) - A_{eff}(\varepsilon_e + 0.5kT_e)\sum n_+ u_{B+}$$
$$+A_{eff}kT_e \cdot ln\left[\frac{(A_{eff}/A)\sum n_+ u_{B+}}{(n_e/4)v_{e,th}}\right]\cdot\sum n_+ u_{B+} \tag{14}$$

2.4 Gas energy balance

In high density discharges, it is well known that plasma heating of the gas can result in high gas temperatures [6,7]. We write a gas energy balance in order to predict the gas temperature:

$$\rho V c_p \frac{dT_g}{dt} = (\dot{m} c_p T_g)_{in} - \dot{m} c_p T_g + 3(m_e / m) \nu_{el} V n_e k (T_e - T_g)$$

$$+ \nu_{ce} V n_+ 3/2 k (T_+ - T_g) + V \sum_i \bar{h}_i M_i \sum_j R_{ij}$$

$$- UA(T_g - T_a) \qquad (15)$$

Here c_p is mixture specific heat, $\bar{h}_i$ is species enthalpy per unit mass, ν_{ce} is charge exchange collision frequency, T_+ is ion temperature, U is an overall heat transfer coefficient, and T_a is ambient temperature. The terms in eqn (15) represent sensible heat associated with gas inflow and outflow, heat gain due to electron-gas elastic collisions, heat gain from charge exchange collisions with ions, heat of all other chemical reactions, and finally, heat loss to the ambient, respectively. The last term is written using an overall transfer coefficient [8] since the wall temperature is unknown. Representing the heat transfer process by a series of resistance network, the overall coefficient is given by

$$U = \frac{1}{1/h_i + \Delta x / K + 1/h_0} \qquad (16)$$

Here, h_i and h_0 are convective heat transfer coefficients for gas-wall and wall-ambient conditions, respectively. The middle term in relation (16) represents conduction through the wall of thickness Δx. K is the thermal conductivity of the wall material. Empirical relations for h_0 can be found in a number of heat transfer texts [8]. We use the following for vertical and horizontal cylinders respectively from ref. 8:

$$h_0 = 1.42\ (\Delta T / L)^{0.25} \qquad (17)$$

$$h_0 = 1.32\ (\Delta T / d)^{0.25} \qquad (18)$$

h_0 is the heat transfer coeffeicient (in W/m^2. deg K) for free convection under laminar flow conditions. Here L is the cylinder length and d is the cylinder diameter; both dimensions must be in meters. ΔT is the temperature difference between the wall and ambient. When wall temperature is unknown, ΔT is taken to be 20 in the first iteration. We can obtain h_i from kinetic theory for conditions encountered in high density discharges. In the case of full thermal accommodation with the wall, the heat transferred by the gas molecules on collision with walls is given by 1/4 $n_g v_{th,g} Ak(T_g - T_w)$ where n_g is gas number density, $v_{th,g}$ is thermal velocity of gas molecules. and T_w is wall temperature. This suggests a relation for h_i as $h_i = 1/4\ kn_g v_{th,g}$. In non-plasma problems, inside heat transfer between the fluid and wall is modeled using Nu = 3.66 for laminar flow, where Nu is the Nusselt number given by $h_i d / K$ [9].

2.5 Summary of equations

For plasma processing problems, SAMPR solves the following equations.

Description	Eqn. Number
Neutral and ion density balances	1
Electron density balance	4
Total mass conservation	3
Plasma power balance	14
Gas energy balance	15
Computation of density	5
Effective area	9, 10

In processing the results, the net reaction rate of each reaction is computed from eqn (2), and plasma potential from eqn (13).

For non plasma problems, the following equations are solved.

Description	Eqn. Number
Neutral species conservation	1
Total mass conservation	3
Gas energy balance	15

An ideal gas law relates density to pressure and gas temperature. Solving for the gas temperature is optional; mass conservation equations alone can be solved for a given temperature, perhaps in a parametric study on the effect of temperature on source gas decomposition and product generation.

2.6 Thermodynamic properties

In the analysis of multicomponent reacting mixtures, data on specific heat c_p, enthalpy H^0 and entropy S^0 are needed. SAMPR requires input of the thermodynamic data in the form of polynomial fits as used in JANNAF [10] and CHEMKIN [11] databases.

$$\frac{c_p}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \tag{19}$$

$$\frac{H^0}{RT} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T} \tag{20}$$

$$\frac{S^0}{R} = a_1 lnT + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \tag{21}$$

Here R is the gas constant and T is the gas temperature. Usually these coefficients are given for two temperature ranges. Hence, there are fourteen coefficients for each species. SAMPR computes mixture-averaged specific heat as

$$c_p = \sum_{i=1}^{I} c_{pi}\ y_{pi} \tag{22}$$

for use in gas energy balance (15). SAMPR uses both JANNAF and CHEMKIN databases; for those species which are not found in either of the databases, the user needs to specify the fourteen coefficients. It is important to mention here that the SAMPR versions distributed outside NASA do not come with either of the databases; it is the responsibility of the users to obtain them from the owners of JANNAF and CHEMKIN.

2.7 Gas phase reactions

The reaction rate of gas phase reactions in nonplasma problems and neutral reactions in plasma problems is given by eqn (2). The forward rate constant is given by

$$k_{fj} = A_j T^{b_j} \exp(-E_j / RT) \tag{23}$$

Here subscript j refers to the reaction. A is the pre-exponent factor and E is the activation energy in cal / mole, and T is the gas temperature in degree K. Pressure dependence of rate constants is not coded now.

The reverse rate constant k_{rj} is related to k_{fj}:

$$k_{rj} = \frac{k_{fj}}{K_{cj}} \tag{24}$$

Where K_c is the equilibrium constant in concentration units. K_c is related to K_p, the equilibrium constant in pressure units, via:

$$K_{cj} = K_{pj}(P_{atm} / RT)^{sum} \tag{25}$$

where

$$\text{sum} = \sum_{i=1}^{I} (\nu''_{ij} - \nu'_{ij}) \tag{26}$$

The equilibrium constant K_p is computed from

$$K_{pj} = \exp\left(\frac{\Delta S_j^0}{R} - \frac{\Delta H_j^0}{RT}\right) \tag{27}$$

Here the Δ denotes computation of difference (products - reactants) in reaction j.

The electron impact reactions are taken to be irreversible and their rate is given by the first term of eqn (2). Note that the rate constant for electron impact reactions need to be expressed as a function of electron temperature T_e.

$$k_j = A_j T^{b_j} \exp(-E_j / RT)$$

Here, A is the pre-exponent factor, E is the activation energy in eV, and T now is the electron temperature in eV. SAMPR also has an option to provide the rate constant data in the form of tables (rate constant vs. mean electron energy ε in eV).

2.8 Surface reactions

The only surface chemistry model available in current version of SAMPR is simple collision of atomic, molecular or ionic species resulting in products. The rate constant in cm/s can be directly specified or via a sticking coefficient, in which case the rate constant is computed from:

$$k_{si} = \nu_i \, (RT / 2\pi M_i) \tag{28}$$

Here subscript i refers to species. k_{si} is rate constant in cm/s, ν_i is sticking coefficient for species i which may be different for the wafer and non-wafer surfaces, T is the gas temperature, M_i is molecular weight of species i, and R is the gas constant.

Positive ions may recombine at a surface typically releasing the corresponding neutral species. The sticking or recombination coefficient may be unity. The rate constant can be computed using eqn (26) except the electron temperature must be used to correspond to Bohm velocity. The effective area correction discussed in relation to eqn (8) and (9) is applied here. Negative ions are usually repelled from the surface and therefore SAMPR assumes the corresponding rate constants to be zero.

2.9 Limitations of SAMPR

It is important to recognize that the 0-d balance equations would reasonably represent physical situations only when the reactor contents are well mixed. Otherwise, the SAMPR results cannot be meaningful. A cold wall CVD reactor is a classic example where 0-d balance equations may not be of much value. The heated wafer has strong temperature gradients in the vicinity of the wafer. Consequently and also due to surface activities, there may be strong gradients of radicals in that region. In any case, a globally-averaged model for the entire reactor may have a temperature too low to trigger any chemical reaction though chemical reactions actively proceed around a volume near the heated wafer. Perhaps, analysis of this small volume may be of some value, at the least to 'sort out' the local chemistry and/or to reduce a large reaction set to a manageable smaller set for use in multidimensional simulations.

In the case of plasma processing, the current version does not include wafer biasing though this can be included in a straightforward manner. (See for example, Wise et al in ref. 12). Also, the correction factors given by eqn (10) apply strictly only to electropositive discharges. They need to be modified for reactive mixtures with a large negative ion population [3].

The surface chemistry model available now is very simple and based on a sticking coefficient formulation. Surface species balance equations are not considered.

Finally, a few other guidelines are worth mentioning. The contribution of the second term in eqn (5) is strong at pressures lower than 5 mTorr. For some reaction sets (both in plasma and nonplasma problems), the coupling of the gas energy equation may result in a stiff set of equations. It may be worthwhile, at first, to fix the temperature at a reasonable value and solve only the species equations (set tsolve = .false. in Read 1); this can be repeated at several temperatures to learn the characteristics.

2.10 Solution of the nonlinear algebraic system of equations generated by the 0-d Model

The 0-d model generates a non-linear system of coupled algebraic equations that is solved by an iterative algorithm. This section describes the iterative algorithm used. The system of equations generated is represented as

$$D(\Phi) + S = 0 \tag{29}$$

where Φ is a vector of the dependent variables (unknowns), D is the non-linear function of the dependent variables, and S represents known source terms that may or may not be present in the system. An iterative scheme is constructed to solve eqn. (29) for Φ.

$$\Phi^{n+1} = \Phi^n + \Delta\Phi^n \tag{30}$$

where n is the iteration index. Equation (29) is linearized about the last iterate for Φ using Taylor series expansion, as follows

$$D(\Phi^{n+1}) = D(\Phi^n) + L(\Phi^n) \cdot \Delta\Phi^n \tag{31}$$

where

$$L(\Phi^n) = \left(\frac{\partial D}{\partial \Phi}\right)^n \tag{32}$$

is the Jacobian matrix of D evaluated at the nth iterate. Equation (29) can be written for the (n+1)th iterate as the linear equation

$$L(\Phi^n)\cdot\Delta\Phi^n = -D(\Phi^n) - S^{n+1} \tag{33}$$

In simplified form, eqn. (33) can be written as

$$L^n\cdot\Delta\Phi = D^n + S^{n+1} \tag{34}$$

Equation (34) can be solved for $\Delta\Phi$ using Gaussian elimination and with eqn. (30) can be used to update the iterate for Φ. This iteration is a Newton scheme that would exhibit quadratic rate of convergence. However, convergence behavior of such a scheme is sensitive to the choice of the initial guess Φ^0. Good initial guesses are difficult to make for the problems encountered here. To overcome the problem, a time-like relaxation parameter is introduced in eqn. (34).

$$(T^{n+1} + L^n)\cdot\Delta\Phi = D^n + S^{n+1} \tag{35}$$

where T is a matrix containing relaxation parameters chosen to ensure convergence of the iteration scheme. Typically, T is a diagonal matrix representing a time-like derivative of Φ.

$$T^{n+1} = diag\{\frac{1}{\Delta t^{n+1}},.....\} \tag{36}$$

where Δt is a time-step parameter. This parameter is varied through the iteration based on the magnitude of $\Delta\Phi$, with limits set for the maximum and minimum values. As the iteration converges and $\Delta\Phi$ decreases, the iteration parameter Δt is increased. Thus the iteration increasingly behaves with convergence like a Newton scheme. Other choices for the matrix T can be made based on the eigenvalue spectrum of the iteration matrix and similar such strategies. Some of these options are available in the computer code.

3. References

1. J.M. Smith, Chemical Engineering Kinetics, McGraw Hill.
2. M. Meyyappan, in Computational Modeling in Semiconductor Processing, edited by M. Meyyappan, Artech House, Boston (1994).
3. C. Lee and M. Lieberman, J. Vac. Sci. Technol. A **13**, 368 (1995).
4. E. Aydil and D.J. Economou, J. Electrochem. Soc. **139**, 1396 (1992).
5. V. Godyak, Nonlocal Bounded Plasma Model With Charge Exchange Collisions, Proceedings of X ESCAMPIG, Orleans (France), edited by B. Dubrevil, European Physical Society (1990).
6. J. Hopwood and J. Asmussen, Appl. Phys. Lett. **58**, 2473 (1991).
7. T. Nakano, N. Sadeghi and R.A. Gottscho, Appl. Phys. Lett. **58**, 451 (1991).
8. J.P. Holman, Heat Transfer, McGraw Hill, New York (1976).
9. W.M. Kays, Convective Heat Transfer, See Table 8.2 on p. 117.
10. JANNAF Thermochemical Tables, Dow Chemical Company (1965).
11. R.J. Kee, F.M. Rupley and J.A. Miller, The Chemkin Thermodynamic Data Base, Sandia Report SAND87-8215B (1991).
12. R.S. Wise, D.P. Lymberopoulos and D.J. Economou, Plasma Sources Sci. Tech. **4**, 317 (1995).
13. M. Meyyappan, Jap. J. Appl. Phys., July 1997.
14. M. Meyyappan, J. Vac. Sci. Tech., **A14**, 2122 (1996).
15. M. Meyyappan and T.R. Govindan, Vacuum, **47**, 215 (1996).
16. M. Meyyappan and T.R. Govindan, IEEE Trans. Plasma Sci., **23**, 623 (1995).

4. SAMPR Program Description

This section describes various subroutines and provides a flow diagram. Also, all the namelist input variables and species/reaction input are explained. A sample input file is given.

4.1 Subroutines

A brief description of the funtionality of each subroutine is given below (arranged in alphabetical order). Additional explanation is also available in the source code at the top of each subroutine; particularly helpful will be the summary of where each routine is called from and the list of routines called from each subroutine.

blkdata	This routine initializes all variables. Also, defines various constants. Called from CSTR
chemsort	This routine processes the reaction information from the input file (alphanumeric input)
cmfrc	This utility routine converts mole fraction to mass fraction. Component molecular weights must be known. Also, returns mixture molecular weight.
cstr	Calls the three routines: blkdata, reada, and exec.
cycsave	This routine saves information during a cycle for pulsed discharges.
depos	This routine computes & prints deposition rate
dxyz	DXYZ constructs linearized terms and loads appropriate coefficients in matrices that are then used to solve the linearized system of equations in an overall procedure to solve the non-linear system of algebraic equations
echem	This routine calculates rate constants for electron impact reactions. Three options are available: direct input, Arrhenius form, and rate constant vs. mean electron energy table.

etch	This routine computes & prints etch rate
exec	This routine has central contol to execute the code (see flow chart)
geneqc	Species mass balance equation, plasma & nonplasma
geneqelt	Electron energy computation from a power balance
geneqt	Gas energy balance
guess	This routine provides initial guess for the solver. For cold start,the input comes from name list. For restart, from a previously converged solution, the input comes from restart file which is fort.19
htcorr	This routine computes heat transfer coefficients for inside heat transfer & heat loss to ambient
intpol	Utility routine; interpolates, given a table of y vs. x
janaftb	This routine reads everything not given via Rdlist. This includes in the following order: species information (alphanumeric input), thermochemical data for those species which are not in JANNAF or CHEMKIN (via a namelist called Janafnl), and finally, reactions (alphanumeric input). Janaftb then calls a few routines to sort out the above information (see flow chart).
lercdb	This routine searches the JANNAF database (or NASA Lewis Research Center database) for thermochemical data
loadc0	This loads coefficients into matrix
loadt	This loads coefficients for time derivatives into matrix
main	Main routine, calls CSTR and prints execution time
matprt	Prints out the matrix for diagnostics purposes

mgausf	Matrix inverter
mxmwrho	This routine calculates mixture molecular weight; also updates total density
nchem	This routine calculates rate constants for neutral reactions and ion chemistry, either direct input or Arrhenius form
output	Prints results
prepare	This routine computes several variables and properties needed prior to defining the nonlinear algebraic equations; called every time step
prtnl	Prints namelist exactly as is and rewinds the file
quick	Called by Matrix inverter, utility routine
ratepr	This routine computes what is called the rate of progress variable rateg(i) for each reaction. When multiplied by appropriate stoichiometric coefficient, this would correspond to the rate of reaction of a given species in gmmole / cm^3s; multiply that by molecular weight for gm / cm^3s.
rdlist	This subroutine reads namelist data
reactp	This routine deals with reaction chemistry, checks consistancy of input reaction data, generates protocol for handling chemistry input
reada	Called from CSTR, preliminary routine which takes care of information generation outside the time loop and prior to the beginning of time loop
remark	Writes a comment to the standard output unit
schem	Computes surface rate constants for neutrals based on sticking coefficient approach
schmion	Computes surface rate constants for ions

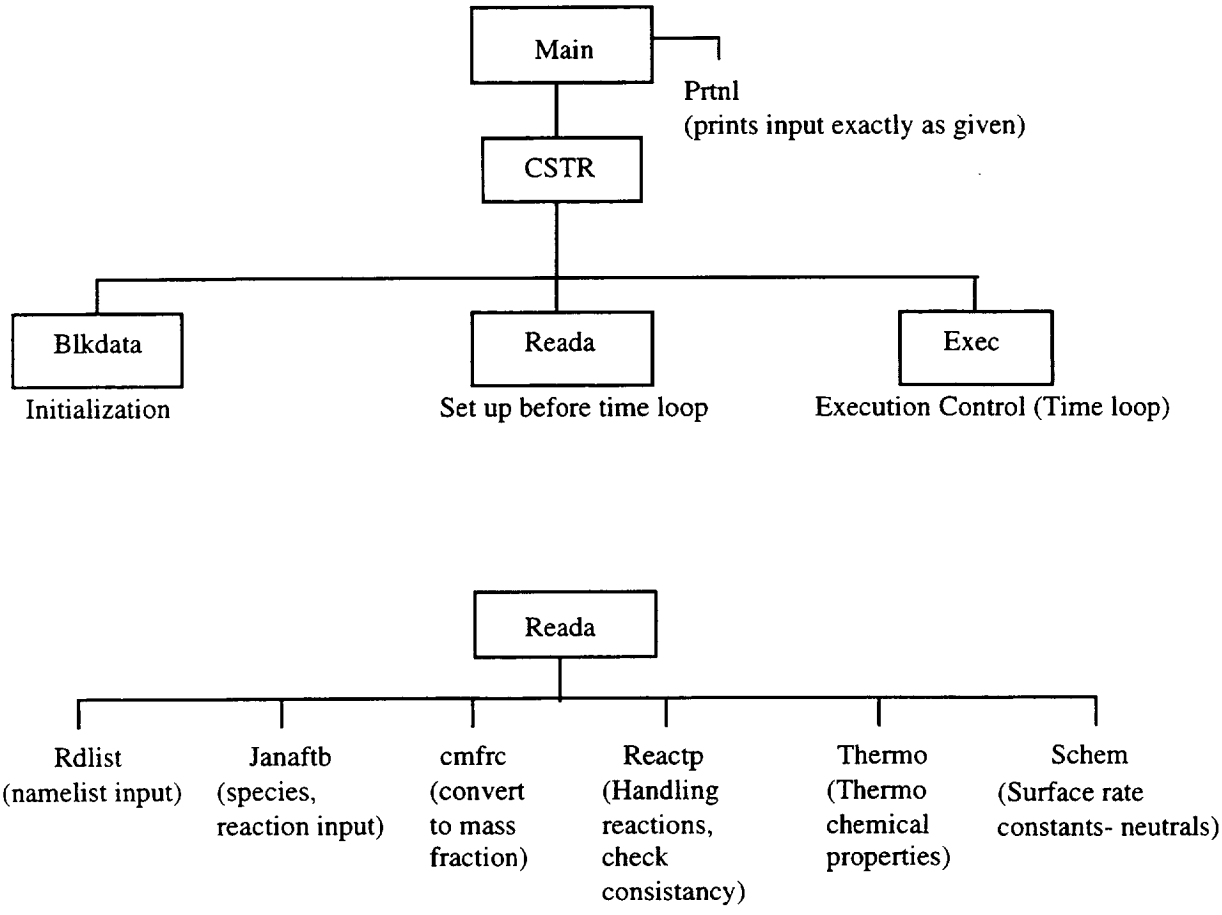
setup	Calls all the balance equations to load coeffiecients into matrix
snldb	Searches CHEMKIN database for thermochemical data
solve	Calls the matrix inverter for solution, convergence check, and computation of residuals
spcoeff	Processes thermochemical data information which may come from JANNAF or CHEMKIN or user specified
specsort	Processes species related information which is given as alphanumeric input
timscl	Provides a few time-scaling options to facilitate rapid convergence for steady-state problems
thermo	This routine computes specific heat, heat of reactions and Gibbs free energy
trange	The thermochemical data is usually for two temperature ranges. This routine computes these ranges
transl	Utility routine which translates character strings to real or integer numbers
trim	Utility routine which returns the length of a string after blanks, nulls and tabs have been removed.

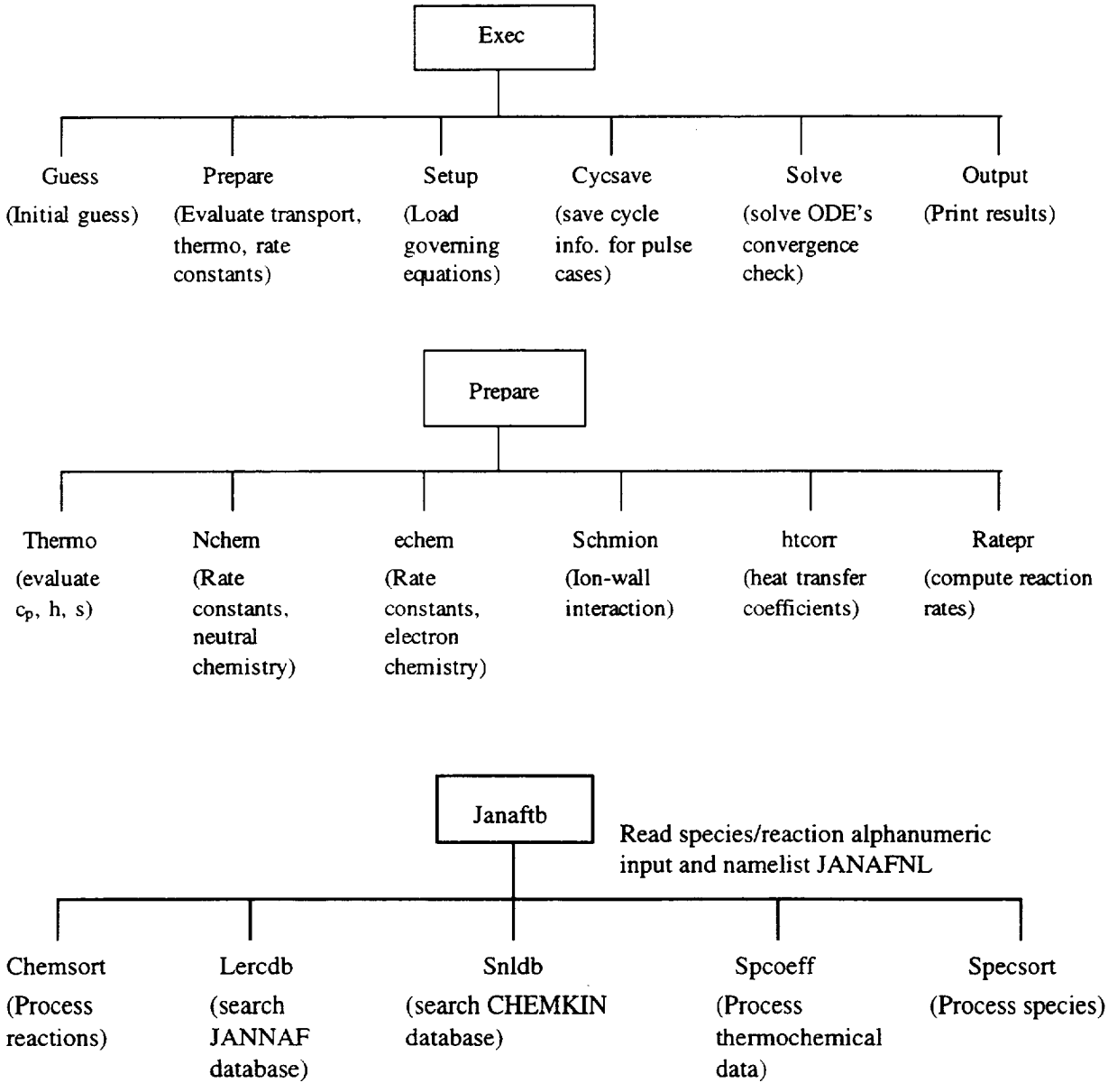
4.2 Flow Chart

The following chart provides an overview of how the code flows. In the source code, see at the top of each routine for entries under:

called from: ???

calles made to ???




Exec
Guess
(Initial guess)
Prepare
(Evaluate transport, thermo, rate constants)
Setup
(Load governing equations)
Cycsave
(save cycle info. for pulse cases)
Solve
(solve ODE's convergence check)
Output
(Print results)
Prepare
Thermo
(evaluate c_p, h, s)
Nchem
(Rate constants, neutral chemistry)
echem
(Rate constants, electron chemistry)
Schmion
(Ion-wall interaction)
htcorr
(heat transfer coefficients)
Ratepr
(compute reaction rates)
Janaftb
Read species/reaction alphanumeric input and namelist JANAFNL
Chemsort
(Process reactions)
Lercdb
(search JANNAF database)
Snldb
(search CHEMKIN database)
Spcoeff
(Process thermochemical data)
Specsort
(Process species)

4.3 Namelist input description

Input to SAMPR is done through namelist except for species and reactions; the latter two can be typed using alphanumeric characterisitics directly. The organization of namelist under various groupings (Read 1, Read 2, Read 3, Read 4, Read 5, Read 6, and Read 7) and explanation of each input parameter are provided below; indeed what follows is a reproduction of the comment cards in routine RDLIST in the source code. Regarding units of various input parameters, use only the units suggested next to each variable.

```
                    READ1 ; WHAT PROBLEM ARE YOU SOLVING?
NAMELIST /READ1/ PLASMA, PULSE, ESOLVE, TSOLVE, IREST

                    READ2 ; REACTOR  RELATED DATA
NAMELIST /READ2/RADIUS,CLENG,NWF,WAREA,IORIENT,NRWALL, CASCADE

                    READ3 ; PROCESS RELATED
NAMELIST /READ3/PRESS,TAMB,TINLT,TEMPGAS,TEMPWF,TEMPWL,
                HEATIN,WALLHT,POWER,PULWID,DUTY,
                ELDENS,ELTEMP,ELTIN,
                ELFLOW,TION,WALTHK,WALTHC

                    READ4 ; PHYSICAL PROPERTIES, ELASTIC COLLISIONS
NAMELIST /READ4/ECFQ,ECINP,DION,CHEXCR,THCON, GLCORR

                    READ5 ; SURFACE RELATED DATA
NAMELIST /READ5/AMWS,ASURF,BSURF,FDENS,NSPECS,RCPINP,RCONS,
                PWALL,STICK

                    READ6 ; SOLVER RELATED
NAMELIST /READ6/DELDT,DT,DTMIN,DTMAX,DTFAC,IDTADJ,NT,
                NCYC,NTPCYC, ITSCALE,
                IDT,ICYC,TTIME,
                PCNT1,PCNT2,SSEPS,GUESWF
```

READ7 ; PRINTING AND PLOTTING RELATED

NAMELIST /READ7/IACTION,IPRINT,ISSCNT

ALL NAMELIST VARIABLES EXPLAINED BELOW

PLASMA - Logical variable, is it a plasma reactor ? if false, no need to deal with electron impact reactions or electron density/energy balances

PULSE - Logical variable, pulsed plasma

TSOLVE - Are you solving for gas temeperature ? logical variable

ESOLVE - Are you solving for electron properties ? logical variable

IREST - 0 --- Cold start, from scratch

1 --- Restart, from some previously saved run

RADIUS - Reactor radius; cm

CLENG - Reactor length; cm

WAREA - Wafer area; cm**2

NWF - Number of wafers

ORIENT - Reactor orientation ; 1 = vertical, 0 = horizontal. Information used to compute heat transfer coefficient for heat loss to the ambient.

NRWALL - Number of radial walls; information used to apply Lieberman correction to account for the deviation of sheath edge ion density from that at the center.

CASCADE - Logical; True allows analysis of process chamber in downstream reactors; but first do the source chamber analysis whose output will serve as input for the cascading. At present, not automatic; resubmit run for process chamber separately

---

PRESS - Pressure inside the reactor; mTorr

TAMB - Ambient temperature; degree K

TINLT - Inlet temperature; degree K

TEMPGAS - Temperature inside reactor; degree K
If (tsolve) is true, this serves as initial guess.

TEMPWL - Temperature of reactor wall; degree K

TEMPWF - Temperature of wafer; degree K

HEATIN - Heat input, if any; cal /cm^3 s

WALLHT - Wall heating flag, logical

ELDENS - Electron density; cm^{-3}

ELTEMP - Electron mean energy; eV
If (esolve) is true, the above two serve as initial guess.

ELTIN - Electron temperature at inlet; = 0 DEFAULT
Set it for process chamber from source chamber value, if cascading

ELFLOW - Electron inflow rate in cascading problems; sccm input isolated here from the rest of the species input since electron is not recognized as a species

TION - Ion temperature, eV

POWER - Input power for plasma reactor; Watts

PULWID - For pulsed plasma, this is the pulse width or period, seconds

DUTY - Duty ratio, i.e. from t = 0 to t = (duty * pulwid), power is on, and remainder of the period power is off. This is a square wave and so duty is between 0 & 1.0

WALTHK - Wall thickness, cm

WALTHC - Wall thermal conductivity; cal /cm.s.degK

DION - Average value for ion diffusivity; cm^2 / s

ECINP - Input mode for elastic collision frequency

= 1, constant frequency, give ecfq
= 2, ecfq vs. mean energy table, no code at present
= 3, gas density * mobility is constant; value given as ecfq (units : 1/cm.s.V); later collision frequency computed and dumped into ecfq array

ECFQ - Elastic collision frequency, array; (1 / s)

CHEXCR - Charge exchange cross section, array; cm^2

THCON - Gas thermal conductivity, average; cal /cm.s.degK

GLCORR - Logical variable, If (true), gas density computed by taking into account that the electron temperature is different from that of gas according to equation 5. Default is false

---

Next surface chemistry:

Note the following to learn limitations. All reactions are unimolecular collision type (not treated like gas phase chemistry). This means that you cannot do heterogenous catalysis with multiple reactants with this version. No balance equation for solid species/reactants/products available now. Each gas phase species can be consumed in a wall collision or reaction at the wafer; can also be generated as a product from wall collision or surface reaction of another species. Rate expressions are identical for wall collisions and wafer reactions at the wafer; nevertheless use 'pwall' to input wall collision probablity and 'stick' for wafer reactions. This allows you to give different probabilities for the wall and the wafer.

PWALL - Wall recombination coefficient or reacion probablity

STICK - Same as above for reactions at the wafer

RCPINP - Flag for specification of surface rate constant array(i) where i is species # 1 --- specify directly (rcons); 2 --- specify stick/pwall above

RCONS - Surface rate constant; cm/s

NSPECS - Number of surface solid species; = 1 for etching which is the wafer material (reactant) and greater than or equal to 1 for deposition (constituents of grown film; example Si and N in a silicon nitride film)

AMWS - Molecular weight of surface solid species, array(i) i = 1,nspecs

ASURF - Number of molecules of gas phase species j formed when one molecule of gas phase species i collides with the wall or wafer; array (j,i)

BSURF - Number of molecules of solid species k formed (or consumed in case of etching) when one molecule of gas phase. Species i collides with the wall or wafer. Array (k,i); k = 1, nspecs and i = 1, nspecg. Realize, BSURF is used only in post-processing to compute etch/deposition rates since we have no equations for solid species.

FDENS - Density of grown film or etched material; gm/cm^3

DTMIN,DT,
DTMAX - Minimum, current & maximum time steps, all dimesionless, reference time is TAU, which is the residence time given by flow rate at reactor conditions divided by reactor volume.

DTFAC - Scaling factor, array dtfac(neqsm); allows to run different equations at different time steps. > 1.0 is deceleration and < 1.0 is acceleration. Can be used with any ITSCALE below.

ITSCALE - Time scaling options to facilitate rapid convergence for steady state solution; do not use for pulse problems or other transient-accurate solutions.
= 0, default
= 1, scaling based on diagonal element
= 2, scaling based on column norm
= 3, scaling based on row norm.
Try default at first; if there is a problem with convergence, then try any of the other options.

SSEPS - Steady state criterion; When sstest (computed in routine solve.f) for each equation falls below sseps, then convergence is declared.

IDTADJ - Flag to adjust time step during iteration

= 0; Do not adjust, default; also used for pulse problem

= 1; Adjust based on value of sstest in comparison to pcnt1 and pcnt2

DELDT - Ratio for time step adjustment

PCNT1, PCNT2 - Lower and upper limits of sstest before action taken to adjust time step; default is 4 and 6%

NT - Number of timesteps specification (only for non-pulse problems)

NCYC - Number of cycles or pulses for pulsed plasma

NTPCYC - Number of time steps per pulse; then you don't need to give dt, dtmin, and dtmax explicitly; they are computed.

IDT - Running count of time step

ICYC - Running count of cycles for pulsed discharge

TTIME - Running count of time.
When starting a new case from an old case, specify idt = 0, ttime = 0, and icyc = 0, to know exactly how many time steps/cycles etc. are needed for the new case.

GUESWF - Intial guess for mass fractions, array

IACTION - = 1 >>>deposition; = 2 >>>etching

IPRINT - Print solution summary every ' iprint ' steps

ISSCNT - Print time step summary (i.e. convergence history) every ' isscnt ' steps.

Alphanumeric input of species

LOCATION: should follow the last namelist read block (read7 now).

The First card SHOULD BE AS IN THE NEXT LINE:

SPECIES MW FLOW DBASE

Now proceed to list species name, molecular weight, flow rate (sccm) and thermochemical source one species per line. Finish with end statement

Guidelines:

1. upper and lower cases permitted in writing species names.
2. For charged species, use + or - sign right after species name.
3. At present, the following 3 options for thermochemical source:
   Lewis data base : acceptable words > LERC, LEWIS, Lerc, Lewis, lerc, lewis
   Sandia data base: acceptable words > SNL, SANDIA, Snl, Sandia, snl, sandia
   User input : acceptable word > INPUT, input
4. If you use any of the data bases for thermochemical properties, then the name of a species must match the way it is written in that data base; otherwise, the species will not be recognized. For example, Sandia data base recognizes C2H2 while the same is called explicitly acetylene in Lewis data base.
5. If you use above data bases, no need to input molecular weight, simply write a 0; molecular weight will be loaded from the data base.
6. Give inlet flow rate of each species in sccm

Thermochemical data

If Lewis or Sandia data base is chosen, for each species, 7 coefficients are automatically loaded in two temperature ranges. For any species, if the User Input option is chosen, then the information must be given inside the JANAFNL Namelist block which follows species input in the runstream. Also in this block, the location of your database, including full directory pathway must be given

Sample input:

dbloc1 = 'u/wk/meyya/database/lerc.bin.database'

dbloc2 = 'u/wk/meyya/database/snl.ascii.database"

aispec(i,j,k) : k is species number according to the order listed in the species input.
j is 1 or 2
i is 1 thru 7 corresponding to seven coefficients

In the above, dbloc1 is the location of JANNAF database and dbloc2 is the location of Sandia database. In the above example, u/wk/meyya/ database denotes the pathway to directory called database where the two are stored.

Alphanumeric input of reactions, rate constants

LOCATION : Right after janafnl namelist block

FIRST LINE : REACTIONS
LAST LINE : END

IN BETWEEN, TYPE REACTIONS ONE PER LINE, USING ALPHANUMERIC CHARACTERS

GUIDELINES:

1. EACH LINE CONTAINS A REACTION AND INFO. RELATED TO RATE CONSTANT. Denote end of reaction with a colon :

2. use > for forward only; use <> for reversible reaction

3. upper as well as lower case permitted

4. use e or E for electrons

5. use M for three body; give M on both sides of the reaction
CH3 + M <> CH2 + H + M :
Note: The entire gas acts as third body; no other option available now.

6. For multiple species on either side of reaction, use +
   2 H2 + O2 > 2 H2O :

7. For charged species, keep the + or - denoting the charge with species name

   Ar + e > Ar+ + 2e :
   Cl2 + e > Cl- + Cl :

8. Extra blanks are ok anywhere

9. Species name in reactions must be the same as in the Species list

10. Currently, stoichiometric coefficients are integers and no fractions allowed

11. Currently, sum of stoichiometric coefficients of all reactants cannot be > 3

    A + B + C > is ok; A + 2B > is ok;

This applies to the reversible reactions too. This restriction (and fractions unallowed) would be a nuisance only when someone wants to use overall reactions; for elementary reactions, this is not a handicap.

Now, rate constant related input

Continue on the same line after reaction and the colon. Provide these in that order: ir, a, b, c, ie,

eth

Guidelines:

1. Not all of them needed to be input as will be seen below

2. These symbols stand in for actual Fortran variables used in the code which may be too long to type in every line (which are RCINP, PREXP, TEXP, EACT, ETHINP, ETH)

3. ir denotes a flag for the type of rate constant input; Corresponding fortran variable is RCINP
   ir is 1 or 2 or 3 ; default is 1
   ir = 1 ; constant rate constant; give only a (see below).
   = 2 ; Arrhenius expression; give a, b, and c (see below).
   if b is zero, omit; no need to say b=0.0
   Expression for k is: a * T**b * exp (-c / RT)
   We use T in deg. Kelvin for neutrals and eV for electrons.
   Also, for electrons, we use kT instead of RT where
   k is Boltzmann constant and R is gas constant.
   = 3 ; for electron impact reactions only; rate constant vs. mean electron energy (eV) table;
   give the name of the file containing the table with exact location)

Example:

Ar + e > Ar* + e : ir = 3 input = /usr/people/meyya/ecr/arg.excit
arg.excit is the name of the file; the rest denotes pathway to the directory.
Format of this file:
you may have comment cards at the top; put them in single quote. The first entry should be the number of data points in the table. Follow this with a 2 column format of energy vs rate constant with one pair per line.

4. a denotes pre-exponential factor (Fortran variable : PREXP). Its units depends on sum of stoichiomeric coefficients of all reactants (for elementary reactions); say this is n.
For neutrals reactions, units in terms of cm**3, gmmole, s
Units : (1/s)(cm**3 / gmmole) ** (n-1)
For electron impact reactions, specify in cm**3 / s
default value : a = 0.0

5. b denotes exponent for T in the Arrhenius expression
Fortran Varable (TEXP); default b = 0.0

6. c denotes activation energy. default c = 0.0
Units : cal / gmmole for neutral reactions
eV for electron impact reactions.

7. ie and eth are related to threshold energy (for electron impact reactions only) to compute energy loss after every inelastic collision.
Corresponding Fortran variables are ETHINP and ETH
ie = 1 or 2 ;
= 1; specify ETH in eV
= 2; means energy loss is 3/2 kT_e (ex: attachment reaction) no need to give ETH then.
default ie = 0 meaning ETH = 0.0

8. Sample input

Ar + e > Ar+ + 2e : ir = 1 a=1.0e-10 c=15.7 ie=1 eth=15.7

ok to have blanks on either side of =
= sign is a must
no need for commas to separate entries; just leave a blank

5. Sample Input and Output Files

Execution of SAMPR using a given input file (for example, argon. nl given below) will create a print file (called argon. prt), file called fort. 20 which contains the solution in a binary form, and a file, fort. 25 which prints out several computed quantities (useful during diagnostics).

If you do pulsed plasma problems, in addition you will get fort.50 which contains all number densities (in the same order as in species list), gas temperature, electron density, and electron temperature at every time step during the pulse. Fort. 51 is a similar file for all the rates of reactions (in the same order as in the reaction list). These two files can be used with any line plotter for plotting time variation during a pulse.

Note if you want to restart a new case from an old case (or doing the same case with few time steps a run thus restarting from previous run), copy or move fort. 20 to fort. 19 since the code reads off of unit 19 and writes into unit 20.

Sample input: argon. nl.

This sets up a case of a high density argon plasma at 3 Torr with 150 W power. Steady solution is desired.

Sample print out follows the listing of argon. nl. Note that SAMPR output reproduces the input exactly as is for verification.

Finally, references 13-16 discuss results from the 0-d analysis using SAMPR and its earlier versions.

```
$READ1
 esolve = .true.,
 tsolve = .true.,
$END
$READ2
 radius = 7.0,
 cleng  = 25.0,
 nwf    = 0,
 warea  = 0.0,
 nrwall = 1,
$END
$READ3
 press  = 3.0,
 power  = 150.0,
 tempgas  = 450.0,
 tempwl = 323.0,
 tempwf = 373.0,
 tinlt = 300.0,
 eldens = 2.0e11, eltemp = 3.6, eltin = 0.0,
$END
$READ4
 ecinp(1) = 3,
 ecfq(1) = 9.66e21,
 chexcr(2) = 3.5e-15,
 thcon = 5.0e-5,
 glcorr = .true.,
```

```
$END
$READ5
  pwall(2) = 1.0,1.0,
  asurf(1,2) = 1.0, asurf(1,3) = 1.0,
$END
$READ6
 nt = 1000, dtmin = 1.0e4 , dt = 1.0e4, dtmax = 1.0e4,
         dtfac(4) = 1.0e6,1.0e6,
 gueswf(1) = 0.98,0.50e-2,1.0e-3,
$END
$READ7
 isscnt = 10,
$END
SPECIES   MW     FLOW   DBASE
    Ar      40.0    15.0    input
    Ar+     40.0    0.0     input
    Ar*     40.0    0.0     input
END
$JANAFNL
 aispec(1,1,1) = 2.5,
 aispec(1,2,1) = 2.5,
 aispec(1,1,2) = 2.5,
 aispec(1,2,2) = 2.5,
 aispec(1,1,3) = 2.5,
 aispec(1,2,3) = 2.5,
$END
REACTIONS
```

Ar + e > Ar* + e : ir = 2 a = 3.712e-8 c = 15.06 ie = 1 eth=11.6

Ar + e > Ar+ + 2e : ir = 2 a = 1.235e-7 c = 18.687 ie = 1 eth=15.7

Ar* + e > Ar + e : ir = 1 a = 2.0e-7

Ar* + e > Ar+ + 2e : ir = 2 a = 2.053e-7 c = 4.95 ie = 1 eth = 4.1

Ar* + Ar* > Ar + Ar+ + e : ir = 1 a = 3.734e14

END

```
**********************************************
*                                            *
*                  S A M P R                 *
*                                            *
*  SIMPLE ANALYSIS OF MATERIALS PROCESSING   *
*  -         -         -         -           *
*                  REACTORS                  *
*                  -                         *
*                                            *
*            VERSION 1.0  JAN. 02, 1997      *
*                                            *
**********************************************
```

1

```
 $READ1
  esolve = .true.,
  tsolve = .true.,
 $END
 $READ2
  radius = 7.0,
  cleng  = 25.0,
  nwf    = 0,
```

```
 warea  = 0.0,
 nrwall = 1,
$END
$READ3
 press  = 3.0,
 power  = 150.0,
 tempgas  = 450.0,
 tempwl = 323.0,
 tempwf = 373.0,
 tinlt = 300.0,
 eldens = 2.0e11, eltemp = 3.6, eltin = 0.0,
$END
$READ4
 ecinp(1) = 3,
 ecfq(1) = 9.66e21,
 chexcr(2) = 3.5e-15,
 thcon = 5.0e-5,
 glcorr = .true.,
$END
$READ5
  pwall(2) = 1.0,1.0,
  asurf(1,2) = 1.0, asurf(1,3) = 1.0,
$END
$READ6
 nt = 1000, dtmin = 1.0e4 , dt = 1.0e4, dtmax = 1.0e4,
         dtfac(4) = 1.0e6,1.0e6,
 gueswf(1) = 0.98,0.50e-2,1.0e-3,
```

```
$END
$READ7
 isscnt = 10,
$END
SPECIES   MW      FLOW      DBASE
 Ar       40.0      15.0      input
 Ar+      40.0      0.0       input
 Ar*      40.0      0.0       input
END
$JANAFNL
 aispec(1,1,1) = 2.5,
 aispec(1,2,1) = 2.5,
 aispec(1,1,2) = 2.5,
 aispec(1,2,2) = 2.5,
 aispec(1,1,3) = 2.5,
 aispec(1,2,3) = 2.5,
$END
REACTIONS
    Ar  + e    > Ar* + e  : ir = 2 a = 3.712e-8  c = 15.06  ie = 1 eth=11.6
    Ar  + e    > Ar+ + 2e : ir = 2 a = 1.235e-7  c = 18.687 ie = 1 eth=15.7
    Ar* + e    > Ar  + e  : ir = 1 a = 2.0e-7
    Ar* + e    > Ar+ + 2e  : ir = 2 a = 2.053e-7  c = 4.95  ie = 1 eth = 4.1
    Ar* + Ar*  > Ar  + Ar+ + e : ir = 1 a = 3.734e14
END
```

SPECIES INFORMATION

==========

NO. SPECIES SYMBOL MOLEC. WT. REF. MASS FRAC REF. FLOW DATA SOURCE CHARGE H298(cal/mole)

--- ---------- ---------- ---------- ---------- ---------- --------- ----------

1 AR 40.000 1.000000E+00 1.500000E+01 INPUT

0 1.481060E+03

2 AR+ 40.000 0.000000E+00 0.000000E+00 INPUT

1 1.481060E+03

3 AR* 40.000 0.000000E+00 0.000000E+00 INPUT

0 1.481060E+03

THERMOCHEMICAL DATA FIT INFORMATION

==========

$$CP(I)/R = A1(I) + A2(I)*T + A3(I)*T**2 + A4(I)*T**3 + A5(I)*T**4$$

$$H(I)/RT = A1(I) + A2(I)*T + A3(I)*T**2 + A4(I)*T**3 + A5(I)*T**4 + A6(I)$$

$$\frac{\quad}{2} \quad \frac{\quad}{3} \quad \frac{\quad}{4} \quad \frac{\quad}{5} \quad \frac{\quad}{T}$$

$$S(I)/R = A1(I)*LN(T) + A2(I)*T + A3(I)*T**2 + A4(I)*T**3 + A5(I)*T**4 + A7(I)$$

----- ----- -----

2 3 4

SPECIES AR - INFORMATION GENERATED BY USER INPUT

THIGH A1 A2 A3 A4 A5 A6 A7 TLOW

----- -- -- -- -- -- -- -- ----

10000.00 2.50000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 5000.00

5000.00 2.50000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 1000.00

1000.00 2.50000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 300.00

300.00 2.50000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00

SPECIES AR+ - INFORMATION GENERATED BY USER INPUT

THIGH A1 A2 A3 A4 A5 A6 A7 TLOW

----- -- -- -- -- -- -- -- ----

10000.00 2.50000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 5000.00

5000.00 2.50000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 1000.00

1000.00 2.50000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 300.00

300.00 2.50000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00 0.00

SPECIES AR* - INFORMATION GENERATED BY USER INPUT

THIGH	A1	A2	A3	A4	A5	A6	A7	TLOW
10000.00	2.50000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	5000.00
5000.00	2.50000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	1000.00
1000.00	2.50000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	300.00
300.00	2.50000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00

REACTION RATE COEFFICIENTS

K(T) = A T**B EXP(-C/T)

#	IR	A	B	C	PIE	ETH
1	2	3.7120E-08	0.000	15.06	1	1.16000E+01
2	2	1.2350E-07	0.000	18.69	1	1.57000E+01

3	1	2.0000E-07	0.000	0.00	0	0.00000E+00
4	2	2.0530E-07	0.000	4.95	1	4.10000E+00
5	1	3.7340E+14	0.000	0.00	0	0.00000E+00

LIST OF CHEMICAL REACTIONS

==========

#	REACTION
1	1.0 AR + 1.0 e ---> 1.0 AR* + 1.0 e
2	1.0 AR + 1.0 e ---> 1.0 AR+ + 2.0 e
3	1.0 AR* + 1.0 e ---> 1.0 AR + 1.0 e
4	1.0 AR* + 1.0 e ---> 1.0 AR+ + 2.0 e
5	2.0 AR* ---> 1.0 AR + 1.0 AR+ + 1.0 e

TIME STEP NO. = 10 TIME = 1.00000E+05 DT = 1.00000E+04

IEQ	SOLUTION	MAX CHANGE	RESIDUAL
1	9.95444E-01	-4.11901E-05	4.13313E-02
2	2.82381E-03	3.31139E-05	3.14185E-02
3	1.73243E-03	8.07618E-06	9.91278E-03

4	1.45007E+00	1.38578E-03	2.86767E-03
5	3.44758E-01	4.65166E-04	2.81376E-02

ELEC. DENSITY = 1.4805993E+11

TIME STEP NO. = 20 TIME = 2.00000E+05 DT = 1.00000E+04

IEQ	SOLUTION	MAX CHANGE	RESIDUAL
1	9.95393E-01	6.44705E-07	6.41678E-04
2	2.87349E-03	-6.92980E-07	6.99503E-04
3	1.73378E-03	4.82751E-08	5.78247E-05
4	1.45519E+00	-5.83546E-05	4.15415E-03
5	3.44546E-01	1.65771E-05	3.46294E-04

ELEC. DENSITY = 1.5097252E+11

TIME STEP NO. = 30 TIME = 3.00000E+05 DT = 1.00000E+04

IEQ	SOLUTION	MAX CHANGE	RESIDUAL
1	9.95392E-01	2.77310E-08	2.76797E-05
2	2.87426E-03	-2.19181E-08	2.04919E-05
3	1.73410E-03	-5.81298E-09	7.18787E-06
4	1.45521E+00	-8.32672E-07	1.18014E-05
5	3.44555E-01	-3.72726E-07	2.08538E-05

ELEC. DENSITY = 1.5098048E+11

TIME STEP NO. = 40 TIME = 4.00000E+05 DT = 1.00000E+04

IEQ	SOLUTION	MAX CHANGE	RESIDUAL
1	9.95392E-01	-5.29800E-10	5.27567E-07
2	2.87422E-03	5.45897E-10	5.46180E-07
3	1.73409E-03	-1.60978E-11	1.86128E-08
4	1.45521E+00	4.28989E-08	2.83847E-06
5	3.44555E-01	-1.03831E-08	1.77923E-07

ELEC. DENSITY = 1.5097839E+11

TIME STEP NO. = 50 TIME = 5.00000E+05 DT = 1.00000E+04

IEQ	SOLUTION	MAX CHANGE	RESIDUAL
1	9.95392E-01	-1.76385E-11	1.76090E-08
2	2.87422E-03	1.35582E-11	1.25684E-08
3	1.73409E-03	4.07956E-12	5.04055E-09
4	1.45521E+00	4.48390E-10	1.67278E-08
5	3.44555E-01	2.89686E-10	1.49963E-08

ELEC. DENSITY = 1.5097840E+11

TIME STEP NO. 55 TIME = 5.50000E+05 DT = 1.00000E+04

IEQ	SOLUTION	MAX CHANGE	RESIDUAL
1	9.95392E-01	1.96695E-13	2.01623E-10
2	2.87422E-03	2.79469E-13	3.83966E-10
3	1.73409E-03	-4.77164E-13	5.85589E-10
4	1.45521E+00	8.65597E-11	1.05843E-08
5	3.44555E-01	-6.26371E-11	2.12356E-09

********* STEADY STATE REACHED *********

INLET CONDITIONS

#	SPECIES	MASS FRACTION	MOLE FRACTION
1	AR	0.1000000E+01	0.1000000E+01
2	AR+	0.0000000E+00	0.0000000E+00
3	AR*	0.0000000E+00	0.0000000E+00

INITIAL TOTAL NUMBER DENSITY = 9.6563997E+13 cm**-3

INITIAL GAS DENSITY = 6.4130165E-09 gm/cm**3

MASS IN FLOW = 4.4640205E-04 gm/s

GAS PHASE RATE CONSTANTS

REACTION #	FORWARD	REVERSE
1	7.0841407E+01	0.0000000E+00
2	8.2258627E+01	0.0000000E+00
3	3.0195679E+04	0.0000000E+00
4	7.3685443E+03	0.0000000E+00
5	3.7340000E+14	0.0000000E+00

FINAL REACTION RATES gmmole cm**-3 s**-1

REACTION #	FORWARD	REVERSE	NET
1	6.1498279E-09	0.0000000E+00	6.1498279E-09
2	7.1409705E-09	0.0000000E+00	7.1409705E-09
3	4.5666662E-09	0.0000000E+00	4.5666662E-09
4	1.1143873E-09	0.0000000E+00	1.1143873E-09
5	8.5404988E-12	0.0000000E+00	8.5404988E-12

WALL COLLISION RATE CONSTANTS cm s**-1

0.0000000E+00 2.8811509E+05 1.0337017E+04

RATE CONSTANTS FOR WAFER REACTIONS cm s**-1

0.0000000E+00 0.0000000E+00 0.0000000E+00

FINAL REACTOR RESULTS

#	SPECIES	MASS FRACTION	MOLE FRACTION
1	AR	0.9953917E+00	0.9925389E+00
2	AR+	0.2874221E-02	0.2865984E-02
3	AR*	0.1734094E-02	0.1729124E-02

SUM OF MASS FRACTION CHECK = 1.000000

OUTFLOW IN sccm FOR CASCADING

SPECIES	MW	FLOW	DBASE
AR	40.00	21.16	INPUT
AR+	40.00	0.06	INPUT
AR*	40.00	0.04	INPUT

ELECTRON OUTFLOW = 6.1088385E-02 sccm

TOTAL OUTFLOW RATE = 2.1314981E+01 sccm

FINAL TOTAL NUMBER DENSITY = 5.2679435E+13 cm**-3

FINAL GAS DENSITY = 3.4885244E-09 gm/cm**3

MASS OUT FLOW = 4.4640205E-04 gm/s

MASS GAIN = 2.7105054E-19 gm/s

FINAL SPECIES NUMBER DENSITY cm**-3

AR	5.2286389E+13
AR+	1.5097840E+11
AR*	9.1089291E+10

GAS TEMEPERATURE = 4.3656270E+02 deg. K

VARIOUS GAS ENERGY PROCESSES, cal.s**-1

SENSIBLE HEAT INFLOW = 0.1663294E-01

HEAT GAIN - ELASTIC COLLISIONS = 0.2988893E-01

HEAT GAIN - CHARGE EXCHANGE = 0.2824704E+00

VOLUMETRIC HEAT ADDITION = 0.0000000E+00

WALL HEATING = 0.0000000E+00

TOTAL HEAT INFLOW INTO SYSTEM = 0.3289922E+00

SENSIBLE HEAT OUTFLOW = 0.2420440E-01

HEAT LOSS TO AMBIENT = 0.3047878E+00

HEAT OF REACTIONS = 0.0000000E+00

TOTAL HEAT OUTFLOW FROM SYSTEM = 0.3289922E+00

ELECTRON DENSITY = 1.5097840E+11 cm**-3

ELECTRON TEMPERATURE = 3.4455549E+00 eV

VP minus VF = 1.9279978E+01 Volts

APPLIED POWER DISTRIBUTION, fraction

INELASTIC COLLISION LOSS = 0.4649

ELASTIC COLLISION LOSS = 0.0008

ELECTRON ENERGY OUTFLOW = 0.0001

AMBIPOLAR WALL LOSS = 0.1407

ION POWER DEPOSITION = 0.3935

1

****

ELAPSED TIME, IN SECONDS

	DATE AND TIME	USER	SYSTEM	TOTAL
START OF JOB	Tue Apr 15 16:17:19 1997	0.0036	0.0195	0.0231
END OF JOB	Tue Apr 15 16:17:20 1997	0.0632	0.0212	0.0844

MACHINE NAME orbit

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 1997	Reference Publication

4. TITLE AND SUBTITLE

SAMPR: A Computer Code for Simple Analysis of Materials Processing Reactors

5. FUNDING NUMBERS

199-61-99

6. AUTHOR(S)

M. Meyyappan and T. R. Govindan

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Ames Research Center
Moffett Field, CA 94035-1000

8. PERFORMING ORGANIZATION REPORT NUMBER

A-976523

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA RP-1402

11. SUPPLEMENTARY NOTES

Point of Contact: M. Meyyappan, Ames Research Center, MS 229-3, Moffett Field, CA 94035-1000; (415) 604-2616

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified — Unlimited
Subject Category 29

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

This is the user's manual for a computer code (SAMPR: Simple Analysis of Materials Processing Reactors) that solves zero-dimensional or volume-averaged conservation equations for the analysis of plasma and non-plasma reactors used in semiconductor processing. Species mass, gas energy, and electron energy equations are solved taking into account homogeneous reactions. Surface reactions are also taken into account in the species balance through properly weighting by the surface-to-volume ratio.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Semiconductor processing, Reactor model, Computer code	54
	16. PRICE CODE: A04

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified		